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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> C08F 26/06, 126/06, 26/08, 26/10, 4/12, A61K 31/79, 7/06, 7/11		<b>A1</b>	<b>(11) International Publication Number:</b> WO 00/68282 <b>(43) International Publication Date:</b> 16 November 2000 (16.11.00)
<b>(21) International Application Number:</b> PCT/US00/09065 <b>(22) International Filing Date:</b> 5 April 2000 (05.04.00) <b>(30) Priority Data:</b> 09/307,211 7 May 1999 (07.05.99) US <b>(71) Applicant:</b> ISP INVESTMENTS INC. [US/US]; 818 Washington Street, Wilmington, DE 19801 (US). <b>(72) Inventors:</b> JACHOWICZ, Janusz; 14 Aunt Patty's Lane, Bethel, CT 06801 (US). LIU, Kou-Chang; 11 Drayton Place, Wayne, NJ 07470 (US). MC MULLEN, Roger, L., Jr.; 200 Franklin Street, Bloomfield, NJ 07003 (US). WINKLER, Thomas; 45 Belle Avenue, Maywood, NJ 07607 (US). <b>(74) Agents:</b> MAUE, Marilyn, J. et al.; International Specialty Products, 1361 Alps Road, Wayne, NJ 07470 (US).			<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> CONDITIONING/STYLING TERPOLYMERS			
<b>(57) Abstract</b> <p>What is described herein are conditioning/styling terpolymers of vinylpyrrolidone (VP), dimethylaminopropyl methacrylamide (DMAPMA) and C<sub>9</sub>-C<sub>24</sub> alkyl dimethylamino-propyl methacrylic acid quaternized monomers (QDMAPMA), in a defined compositional range. Hair and skin care compositions which include these terpolymers exhibit advantageous low tackiness and high humidity resistance.</p>			

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## CONDITIONING/STYLING TERPOLYMERS

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention relates to polymers for use in hair and skin care compositions, and, more particularly, to conditioning and styling terpolymers having advantageous low tackiness and high humidity resistance.

#### 2. Description of the Prior Art

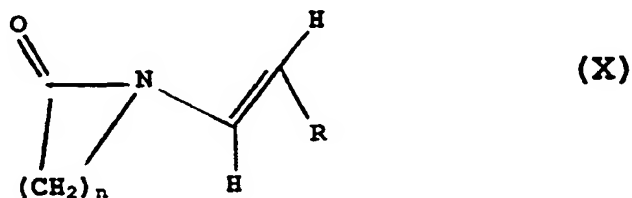
Copolymers of VP and DMAPMA have been used extensively as active components of hair and skin compositions. While these copolymers are generally suitable polymers for such products as conditioners and shampoos, it is desired to provide new polymers having improved performance characteristics in these and other personal care products.

### SUMMARY OF THE INVENTION

What is described herein is a terpolymer of vinylpyrrolidone (VP), dimethylaminopropyl methacrylamide (DMAPMA) and C<sub>9</sub>-C<sub>24</sub> alkyl dimethylaminopropyl methacrylic acid quaternized monomers (QDMAPMA), within a defined compositional range, for use in hair and skin care compositions, which are characterized by low tackiness and high humidity resistance.

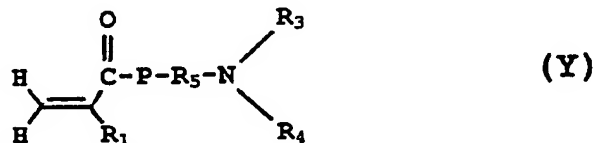
DETAILED DESCRIPTION OF THE INVENTION

The terpolymers of the invention comprises the following X, Y, and Z monomers, having the formulas given below:



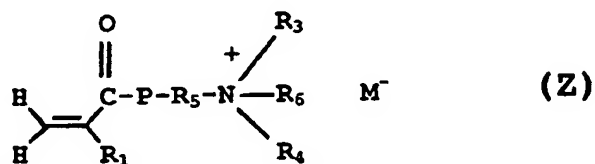
where:

X is a vinyl cyclic amide, e.g. vinyl pyrrolidone;  
 $n = 3$  to  $6$ ; R is H or  $C_1$ - $C_5$  alkyl and wt% of X = 40-95;  
 preferably 60-90;



where:

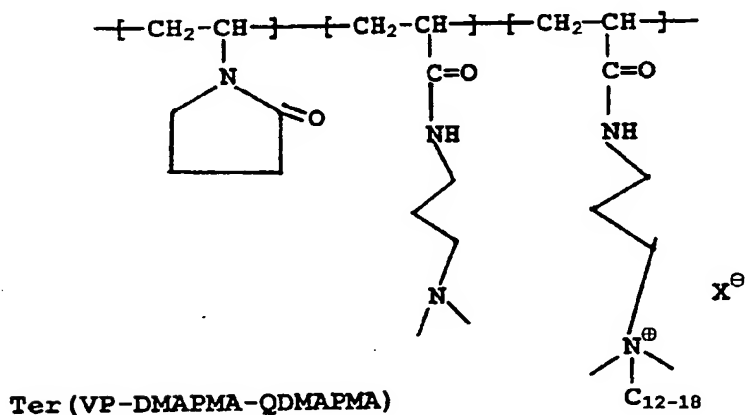
Y is a derivative of acrylic acid; P is O or  $NR_2$ ;  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$  are independently H or  $C_1$ - $C_5$  alkyl;  $R_5$  is  $C_2$ - $C_{16}$  alkyl alkylene; and wt% of Y = 0.1 to 55; preferably 5-30;



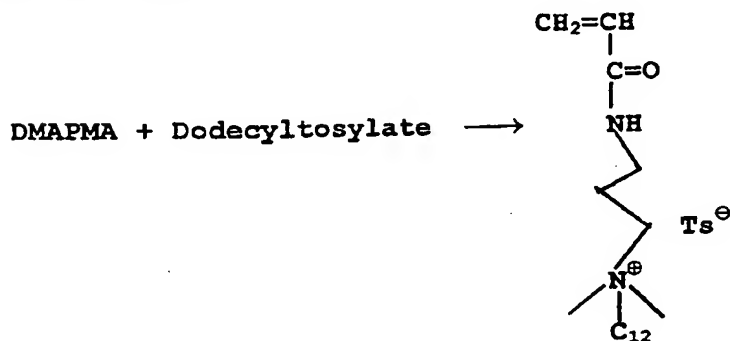
where:

Z is a quaternized derivative of an acrylic acid; P is O or NR<sub>2</sub>; R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> are independently H or C<sub>1</sub>-C<sub>5</sub> alkyl; R<sub>5</sub> is a C<sub>2</sub>-C<sub>16</sub> alkylene; and R<sub>6</sub> is C<sub>9</sub>-C<sub>24</sub> alkyl; M is a halide, tosylate or phosphate anion; and wt% of Z = 0.25 to 50, preferably 1-30.

The terpolymers of the invention are hydrophobically-modified cationic polymers having long alkyl-chains therein. A typical terpolymer thus has the following formulas:



Suitably, monomer Z is prepared by tosylating DMAPMA as follows:



In preferred embodiments of the invention,  
X is vinyl pyrrolidone;  
Y is dimethylaminopropyl methacrylamide, and  
Z is a C<sub>12</sub>-C<sub>18</sub> alkyl quaternized derivative of an acrylic acid;

X is about 60-90 wt%, Y is about 5-30 wt% and Z is about 1-30 wt%; Z is C<sub>12</sub> alkyl quaternized monomer; the weight average molecular weight of the terpolymer is 200,000 to 2,000,000; preferably 400,000 to 800,000; it is water soluble or water dispersible; and forms a clear humidity resistant, hydrophobic film when cast upon a support surface; which is surface active and hydrolytically stable; and is a homogeneous terpolymer.

Cosmetic compositions of advantageous properties including about 0.1 to 10% by weight of the terpolymer can be prepared conveniently in this invention.

Preferably, the homogeneous terpolymers of the invention are made according to the method described by Kou-Chang Liu et al. in U.S. Patent 5,626,836.

#### EXAMPLE 1

The preparation of (dodecyldimethyl methacryloimidopropyl ammonium tosylate). [DMAPMA-C<sub>16</sub>Ts]  
A mixture of 360 g of dodecyl tosylate and 200 g of DMAPMA were slowly heated up to 70°C without a solvent. Stirring was continued at 70°C for 2 hours. Then the reaction was cooled to room temperature and solidified product was further used in polymerization without purification.

EXAMPLE 2Terpolymer of VP/DMAPMA/DMAPMAA-C<sub>12</sub>Ts Quat

N-Vinylpyrrolidone (VP) (280 g) and deionized water (1400 g) are charged into a 2-liter resin pot equipped with a gas inlet, liquid inlet, a thermometer, and a condenser. The pH of the solution is adjusted to about 7.5 with KOH. Then a stream of nitrogen is introduced which bubbles through the solution during the reaction. The solution is gradually heated to 65°C for Lupersol® 11 catalyzed reaction, or to 78°C for a Vazo® 67 initiated process. Then, DMAPMA (17.5 g) and DMAPMAA-C<sub>12</sub>Ts quat (52.5 g) are added continuously and uniformly into the pot with vigorous stirring for 4 hours so that the relative concentrations of the monomeric VP, DMAPMA, and DMAPMAA-C<sub>12</sub>Ts quat monomer remain practically constant throughout the reaction at predetermined levels.

As soon as DMAPMA and the DMAPMAA-C<sub>12</sub>Ts quat are introduced into the pot, Lupersol® 11 (t-butylperoxy pivalate in mineral spirits) or Vazo® 67 2,2-azobis(2-methylbutanenitrile), catalyst is added. The rate of the addition of the catalyst is such that 2 ml of Lupersol is completely delivered in 4 hours. Then the solution is held for an additional 3 hours at 68°C (or 78°C for Vazo 67 initiator). The product is an aqueous solution of a homogeneous terpolymer of VP, DMAPMA and a DMAPMAA-C<sub>12</sub>Ts quat has a predetermined composition indicative of the relative amounts of each monomer used in the process and is substantially free of any residual homopolymer or copolymer. The yield of the terpolymer product is substantially quantitative.

EXAMPLES 1-6  
Terpolymers of VP/DMAPMA/QDAPMAA-DTs  
(Dodecyl Tosylate Hydrophobe)

Ex.	Composition (wt%) VP/DMAPMA/ QDAPMAA-DTs	Conc % w/w	M <sub>n</sub> x10 <sup>3</sup>	D	η x10 <sup>3</sup> [cps]	Resid VP [ppm]	Resid DMAPMA [ppm]	Resid HDMAPMA %C <sub>12</sub> OH
1	74/19.3/6.7	10	540	4.7	117	210	<100	0.34
2	74/19.3/6.7	15	560	4.6	163	640	<100	0.58
3	74/19.3/6.7	10	550	4.6	34.6	640	<100	0.58
4*	80/71/12.9	20	-	-	41.4	-	-	-
5*	80/10.36/9.64	20	-	-	35	-	-	-
6*	77/20/3	20	-	-	26.8	-	-	-

\* Vazo 67 initiator used

EXAMPLE 7  
Preparation of cocoyldimethyl  
methacrylamidopropyl ammonium tosylate

A mixture of 284.4 g of C<sub>16</sub>-C<sub>18</sub> tosylate and 126.7 g of DMAPMA were slowly heated up to 70°C without a solvent. Stirring was continued at 70°C for 3 hours. Then the temperature was raised to 80°C and maintained for 6 hours while stirring. Then the reaction was cooled to room temperature and solidified product was further used in polymerization without purification.



EXAMPLE 8Terpolymer of VP/DMAPMA/DMAPMAAC<sub>16</sub>-C<sub>18</sub>Ts Quat.

The copolymerization of VP/DMAPMA/DMAPMAA-C<sub>16</sub>Ts Quat followed the same procedure as given in Example 2.

EXAMPLES 8-10Polymers of VP/DMAPMA/DMAPMAA-C<sub>16</sub>Ts(Hexadecyl Tosylate Hydrophobe)

Ex.	Composition (wt%) VP/DMAPMA/ DMAPMAA-C <sub>16</sub> Ts	Conc.
		% w/w
8	74/19.3/6.7	15
9	74/20/6	20
10	77/20/3	20

EXAMPLE 11Preparation of Lauryl-Dimethyl  
Methacrylamidopropyl Ammonium Chloride

A mixture of 350 g of DMAPMA and 280 g of chlorododecene (1.5:1) was stirred with 111.2 g of water (15%) and 6 drops of concentrated sulfuric acid. The reaction mixture was heated up to 95°C and N<sub>2</sub> was bubbled through it. The conversion was followed by GC. After 24 hours the reaction mixture was cooled off (95% conversion of vinyl chloride) and product was further used in polymerization without purification.

EXAMPLES 12-17Terpolymer of VP/DMAPMA/QDMPMA Lauryl Chloride

The terpolymerization of VP/DMAPMA/DMPMAA-C<sub>16</sub> Cl quat followed the same procedure as described in Example 2.

Ex.	Composition (wt%) VP/DMAPMA/ QDMPMAA-LCL	Conc % w/w	M <sub>n</sub> 10 <sup>3</sup>	D	η x10 <sup>3</sup> [cps]	Resid VP [ppm]	Resid LCLA [ppm]
12	77/70/3	20	615	5.5	28	600	400
13	74/70/6	20	510	5.4	35	600	800
14	71/70/9	20	485	6.2	64	500	1300
15	93.3/3.7/3	20	493	5.3	13	200	400
16	86.5/7.5/6	20	550	6.8	14	400	800
17	79.8/11.2/9	20	575	7.2	30	300	1300

EXAMPLE 18CONDITIONING CREAM RINSE FORMULATIONPart A

86.4% Deionized H<sub>2</sub>O

0.5% SLES (Cerasynt LP; ISP)

0.1% NaEDTA (Ethylenediaminetetraacetic acid disodium salt dihydrate; Aldrich)

Part B

2.55 Cetyl Stearyl Alcohol (Lanette Wax O; Henkel Corporation)

Part C

10% Aculyn 46 (modified polyethylene glycol, enzymatically modified starch; Rohm & Haas)

Part D

0.5% Conditioning Additive of Example 13

Instructions

Heat Part A to 60°C with moderately slow stirring. Add Part B to Part A once Part A appears well mixed and homogeneous. Continue slow stirring and allow solution to cool to an ambient temperature. Add Part C while stirring and eventually add Part D.

EXAMPLE 19CONDITIONING SHAMPOO FORMULATIONPart A

15% Ammonium Lauryl Sulfate (Standapol A, Henkel Corporation)

15% Sodium Lauryl Sulfate (Rhodapon SB-8208/S, Rhône Poulenc)

8% Cocamidopropyl Betaine (Mitratine CB, Rhône Poulenc)

2% Lauramide DEA (Monamid 716, Mona Industries)

Part B

1% Conditioning Additive of Example 13

58.8% Deionized H<sub>2</sub>O

Part C

0.2% Diazolidinyl Urea/Iodopropynyl Butylcarbamate  
(Germall Plus, ISP)

Instructions

Heat Part A to 60°C with moderately slow stirring for approximately ½ hr. or until solution becomes transparent. At the same time, heat Part B to 55°C while stirring until homogeneous solution is obtained. Add Part B to Part A while continuously stirring. Remove temperature source. Once the resulting solution has reached 45°C, add Part C. Continue to stir (slowly) until the target solution has cooled to an ambient temperature.

In the conditioners and shampoo formulations tested under actual use conditions in comparison with similar formulations with known polymers, the terpolymers of the invention have excellent wet combing, excellent dry feel and softness, and excellent wet feel.

Furthermore they are characterized by excellent styling properties in terms of stiffness, humidity resistance and dry and wet feel.

EXAMPLE 20STYLING LOTION

A styling lotion formulation was prepared in aqueous solution using 1% by weight of the terpolymer of Example 1 and 0.1% preservative.

EXAMPLE 21  
STYLING MOUSSE

A concentrate is prepared by dissolving 1 g of the terpolymer of Example 1, 0.1 g of preservative and 98.9 g of deionized water.

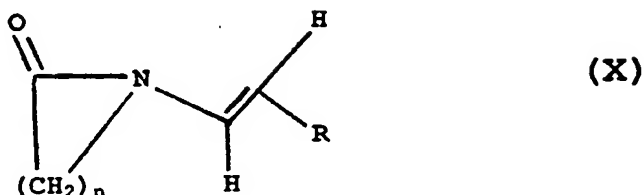
A styling mousse formation is prepared by mixing 70 g of the concentrate and 30 of hydrocarbon propellant in an aerosol can provided with a mousse dispenser.

While the invention has been described with particular reference to certain embodiments thereof, it will be understood that changes and modifications may be made which are within the skill of the art. Accordingly, it is intended to be bound only by the following claims, in which:

## WHAT IS CLAIMED IS:

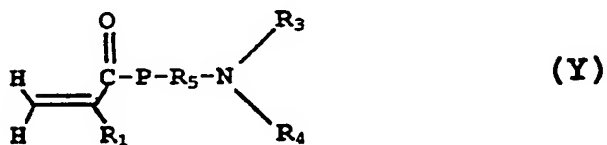
1. A terpolymer comprised of the following monomers;

X, Y and Z;



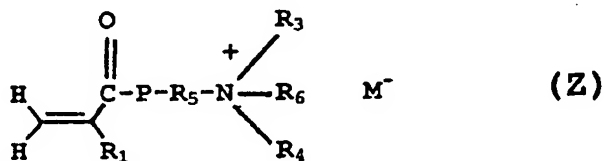
where:

n is 3 to 6; R is H or C<sub>1</sub>-C<sub>5</sub> alkyl and wt% of  
X = 40-95;



where:

P is O or NR<sub>2</sub>; R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> are independently H or C<sub>1</sub>-C<sub>5</sub> alkyl; R<sub>5</sub> is C<sub>2</sub>-C<sub>16</sub> alkyl alkylene; and wt% of  
Y = 0.1 to 55; and



where:

P is O or NR<sub>2</sub>; R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> are independently H or C<sub>1</sub>-C<sub>5</sub> alkyl; R<sub>5</sub> is a C<sub>2</sub>-C<sub>16</sub> alkylene; R<sub>6</sub> is C<sub>9</sub>-C<sub>24</sub> alkyl; M is a halide, tosylate or phosphate anion; and wt% of Z = 0.25 to 50.

2. A terpolymer according to claim 1 wherein:  
X is vinyl pyrrolidone,  
Y is dimethylaminopropyl methacrylamide, and  
Z is a C<sub>12</sub>-C<sub>18</sub> alkyl quaternized derivative of an acrylic acid.
3. A terpolymer according to claim 2 wherein X is about 60-90 wt%, Y is about 5-30 wt% and Z is about 1-30 wt%.
4. A terpolymer according to claim 2 wherein Z is C<sub>12</sub> alkyl quaternized monomer.
5. A terpolymer according to claim 1 wherein the weight average molecular weight is 200,000 to 2,000,000.
6. A terpolymer according to claim 5 wherein said molecular weight is 400,000 to 800,000.

7. A terpolymer according to claim 2 which is water soluble or water dispersible.

8. A terpolymer according to claim 1 which forms a clear humidity resistant, hydrophobic film when cast upon a support surface.

9. A terpolymer according to claim 1 which is surface active and hydrolytically stable.

10. A terpolymer according to claim 1 which is a homogeneous terpolymer.

11. A cosmetic composition including about 0.1 to 10% by weight of the terpolymer of claim 1.

12. A cosmetic composition according to claim 11 which is a hair or skin care product.



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/09065

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : Please See Extra Sheet.

US CL : 526/258, 195, 264; 424/70.12, 78.24

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 526/258, 195, 264; 424/70.12, 78.24

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

West 1.2, Nonpatent literature

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	U.S. 5,997,855 A [LIU] 07 December 1999, abstract, col. 2, lines 48-51, 12-18, col.5, lines 3-6 col.2, lines 50-51, col.3, lines 23-51, col.1, lines 50-55	1,5,6,10-12 ----- 2-4,7-9
A	U.S. 5,321,110 A (SHIH) 14 June 1994	1-12
A	U.S. 5,603,919 A (LIU et al ) 18 February 1997	1-12
A	U.S. 4,956,430 A (TAZI) 11 September 1990	1-12

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

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Date of the actual completion of the international search

23 MAY 2000

Date of mailing of the international search report

27 JUL 2000

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## INTERNATIONAL SEARCH REPORT

International application No.  
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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	U.S. 5,626,836 A (LIU et al) 06 May 1997	1-12

**INTERNATIONAL SEARCH REPORT**

International application No.  
PCT/US00/09065

**A. CLASSIFICATION OF SUBJECT MATTER:**

IPC (7):

CO8F 26/06, 126/06, 26/08, 26/10, 4/12;  
A61K 31/79, 7/06, 7/11